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Reactions of Aziridine and Oxirane with Manganese and Rhenium Carbonyl Complexes. Syntheses of Neutral 5-Membered Cyclic Aminooxy- and Dioxycarbene Compounds

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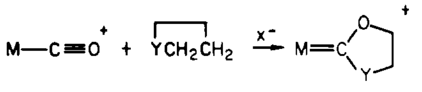
In the presence of a halide ion catalyst, aziridine ($H\overline{NCH_2C}H_2$) and oxirane ($\overline{OCH_2C}H_2$) react with one CO group in $M(CO)_5X$ (M = Mn, Re) to form the corresponding cyclic aminooxy- and dioxycarbene compounds according to

$$M(CO)_5X + \overline{YCH_2C}H_2 \xrightarrow[25\ °C]{Br^-} cis\text{-}M(CO)_4X(\overline{COCH_2CH_2Y})$$

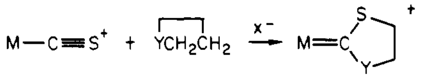
where M = Mn, X = Br and I, Y = NH; M = Mn, X = Cl, Br, and I, Y = O; and M = Re, X = Cl, Br, and I, Y = NH and O. Even in the absence of any added Br^-, $M(CO)_5Br$ reacts with excess $H\overline{NCH_2C}H_2$ in CH_3CN to form the corresponding aminooxycarbene derivatives. On the basis of spectral data, these compounds have been assigned a cis structure. One bis(dioxycarbene) compound, *fac*-$Re(CO)_3Cl(\overline{COCH_2CH_2O})_2$ has also been isolated from the products of the reaction of $Re(CO)_5Cl$ with oxirane. The action of aziridine on $Mn(CO)_5Cl$ in the absence of Br^- yields a substituted product $Mn(CO)_3Cl(H\overline{NCH_2C}H_2)_2$. The IR and ^1H and ^{13}C NMR spectra of the complexes and also general trends in reactivities of $\overline{YCH_2C}H_2$ with metal carbonyl complexes are discussed.

Introduction

Most previously described reactions of the 3-membered heterocycles $\overline{YCH_2C}H_2$, where Y = NH (aziridine), O (oxirane), and S (thiirane), with transition-metal complexes are known to occur at the metal centers.[3-9] Recently, we reported[10,11] that $\overline{YCH_2C}H_2$ reacts in the presence of a halide ion catalyst with CO and CS ligands in certain cationic carbonyl and thiocarbonyl complexes of iron, manganese, and ruthenium to form corresponding cyclic aminooxy-, dioxy-, aminothio-, and dithiocarbene derivatives according to eq 1 and 2.


(1)

M = $CpFe(CO)_2$, $CpRu(CO)_2$, CpMn(CO)(NO), $CpFe(CO)(PPh_3)$; Y = HN, O


(2)

M = $CpFe(CO)_2$; Y = HN, S

In order to explore the possible range of reactivity of $\overline{YCH_2C}H_2$ with metal carbonyls, we have investigated reactions of aziridine and oxirane with CO ligands in the neutral carbonyl complexes of manganese(I) and rhenium(I), $M(CO)_5X$ (X = Cl, Br, I). These reactions, like those reported earlier,[10,11] lead to the generation of cyclic aminooxy- and dioxycarbene derivatives, $M(CO)_4X(\overline{COCH_2CH_2Y})$ (M = Mn, Re; X = Cl, Br, I; Y = NH, O). In this paper we describe the results of these studies and discuss the spectroscopic characterization of the resulting cyclic carbene compounds.

Experimental Section

General Procedures. All preparative manipulations, solvent purifications, and physical measurements (IR, ^1H and ^{13}C NMR, and mp) were performed as described in the previous paper.[11]

Starting Complexes. The compounds $Mn(CO)_5Cl$,[12] $Mn(CO)_5Br$,[13] $Mn(CO)_5I$,[14] $[Mn(CO)_5(CH_3CN)]PF_6$,[15] $[Re(CO)_5(CH_3CN)]PF_6$,[15] and $[Mn(CO)_5(PPh_3)]PF_6$[15] were prepared according to literature methods. The iodo compound $Mn(CO)_5I$ was also prepared from $[Mn(CO)_5(CH_3CN)]PF_6$ by the same procedure as described below for the synthesis of $Re(CO)_5I$. The halopentacarbonylrhenium(I), $Re(CO)_5X$ (X = Cl, Br), was prepared by a slight modification of known methods.[16-18] Chloropentacarbonylrhenium(I), $Re(CO)_5Cl$, was prepared by oxidation of $Re_2(CO)_{10}$ with Cl_2 in CH_2Cl_2 at 0 °C. Starting from 2.0 g (3.1 mmol) of $Re_2(CO)_{10}$, a 2.10-g (96%) yield of $Re(CO)_5Cl$ was obtained on removing the solvent. Similarly, oxidizing 2.0 g (3.1 mmol) of $Re_2(CO)_{10}$ in 50 mL of CS_2 (in a hood) with 0.16 mL (0.50 g, 3.1 mmol) of Br_2 produced 2.3 g (94%) of the colorless microcrystalline compound, $Re(CO)_5Br$. Iodopentacarbonylrhenium(I), $Re(CO)_5I$, was prepared by the action of NaI on $[Re(CO)_5(CH_3CN)]PF_6$.[15] The salt $[Re(CO)_5(CH_3CN)]PF_6$ (1.0 g, 1.9 mmol) was stirred with 0.70 g (4.7 mmol) of NaI in 150 mL of CH_2Cl_2 overnight (16 h) until the IR spectrum of the solution did not reveal a band at 2080 cm^{-1} due to $[Re(CO)_5(CH_3CN)]PF_6$. The mixture was filtered, the residue was washed with CH_2Cl_2, and the filtrate was evaporated under a water aspirator vacuum to yield fine microcrystals that were quickly chromatographed on silica gel by using CH_2Cl_2. Upon removal of the solvent, colorless crystals of $Re(CO)_5I$

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[3] Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 1460.

[4] Scherzer, J.; Phillips, P. K.; Clapp, L. B.; Edwards, J. O. *Inorg. Chem.* **1966**, *5*, 845 and references therein.

[5] Giering, W. P.; Rosenblum, M.; Tancrede, J. *J. Am. Chem. Soc.* **1972**, *94*, 7170.

[6] Beck, W.; Danzer, W.; Hofer, R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 77.

[7] Rakowski-Dubois, M.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245.

[8] Schloter, K.; Beck, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35b*, 985.

[9] Danzer, W.; Fehlhammer, W. P.; Liu, A. T.; Thiel, G.; Beck, W. *Chem. Ber.* **1982**, *115*, 1682.

[10] Singh, M. M.; Angelici, R. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 163; *Angew. Chem. Suppl.* **1983**, 184.

[11] Singh, M. M.; Angelici, R. J. *Inorg. Chem.*, preceding paper in this issue.

[12] Reimer, K. J.; Shaver, A. *Inorg. Synth.* **1979**, *19*, 159.

[13] Quick, M. H.; Angelici, R. J. *Inorg. Synth.* **1979**, *19*, 160.

[14] Quick, M. H.; Angelici, R. J. *Inorg. Synth.* **1979**, *19*, 161.

[15] Drew, D.; Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1975**, *14*, 1579.

[16] Hileman, J. C.; Huggins, D. K.; Kaesz, H. D. *Inorg. Chem.* **1962**, *1*, 933.

[17] Angelici, R. J.; Kruse, A. E. *J. Organomet. Chem.* **1970**, *22*, 461.

[18] Kaesz, H. D.; Bau, R.; Hendrickson, D.; Smith, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 2844.

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were obtained. They were recrystallized from CH_2Cl_2–pentane at −20 °C; yield 0.64 g (74%).

Syntheses of Complexes. $Mn(CO)_4Br(\overline{COCH_2CH_2NH})$ (I). To a stirring solution of 0.20 g (1.0 mmol) of $[BrCH_2CH_2NH_3]Br$ in 10 mL of CH_3CN containing 0.052 mL (1.0 mmol) of aziridine was added 0.28 g (~1.0 mmol) of $Mn(CO)_5Br$. After 1 h an additional 0.04 mL (0.8 mmol, total 1.8 mmol) of aziridine and 0.20 g (1.0 mmol) of $[BrCH_2CH_2NH_3]Br$ were added. When IR spectra of the reaction mixture revealed bands due only to the carbene product, the solution was evaporated to yield an oily yellow mass. It was extracted with excess boiling CH_2Cl_2, filtered, and concentrated under vacuum. On standing at −20 °C for 2 days, this solution produced orange-yellow crystals. The sticky residue left in the reaction flask after the CH_2Cl_2 extraction was extracted with CH_3CN and filtered. The filtrate was evaporated to dryness, and the residue was dissolved in CH_2Cl_2. When pentane was added and the solution allowed to stand at −20 °C, the solution yielded yellow crystals. These crystals and those obtained from the first CH_2Cl_2 crystallization were collected, redissolved in CH_2Cl_2, and recrystallized from CH_2Cl_2–pentane at −20 °C: yield 0.12 g (39%); mp 94 °C. Anal. Calcd for $C_7H_5BrNO_5Mn$: C, 26.44; H, 1.58; N, 4.41. Found: C, 26.33; H, 1.68; N, 4.47.

The same reaction was also carried out without using $[BrCH_2CH_2NH_3]Br$. A solution of 0.27 g (0.99 mmol) of $Mn(CO)_5Br$ in 10 mL of CH_3CN was stirred with 0.07 mL (1.4 mmol) of aziridine added in two equal portions over a time interval of 12 h. After a total of 16 h of stirring, the reaction mixture did not show bands in the IR spectrum due to $Mn(CO)_5Br$. Evaporation of the solvent followed by extraction of the residue with CH_2Cl_2, filtration of the extract through anhydrous $MgSO_4$, and crystallization from CH_2Cl_2–pentane at −20 °C produced 0.26 g (81%) of yellow $Mn(CO)_4Br(\overline{COCH_2CH_2NH})$ crystals. These crystals were, however, found to be contaminated with trace amounts of $Mn(CO)_3Br(\overline{CH_2CH_2NH})_2$ as revealed by IR spectra. No attempts were made to purify compound I prepared by this method.

$Mn(CO)_4I(\overline{COCH_2CH_2NH})$ (II). This compound was prepared by following the same procedure as for I. To a mixture of 0.3 g (1 mmol) of $Mn(CO)_5I$ and 0.19 g (0.93 mmol) of $[BrCH_2CH_2NH_3]Br$ in 20 mL of CH_3CN was added 0.12 mL (2.30 mmol) of aziridine in two equal portions over a time interval of 1 h. After a total reaction time of 4 h, the solvent was removed under reduced pressure. The sticky orange-red residue was chromatographed on a column (70 × 1.2 cm) of silica gel (Kiesel gel 60, 230–400 mesh, EM) in CH_2Cl_2 solvent. The first narrow yellow band contained a trace amount of unreacted $Mn(CO)_5I$ (IR evidence). The major orange-red band was eluted with CH_2Cl_2, evaporated to 20 mL, and finally filtered through a bed of anhydrous $MgSO_4$ to remove any solid particles. The filtrate volume was reduced to ca. 5 mL, and hexane was added. Orange-red crystals of II were obtained by cooling the mixture at −20 °C overnight: yield 0.24 g (66%); mp 50 °C. Anal. Calcd for $C_7H_5INO_5Mn$: C, 23.04; H, 1.30; N, 3.84. Found: C, 23.23; H, 1.30; N, 4.00. The last slow-moving yellow band after elution with CH_2Cl_2 gave a small amount of a yellow product, which according to its IR spectrum was $Mn(CO)_3I(\overline{HNCH_2CH_2})_2$.

$Re(CO)_4Cl(\overline{COCH_2CH_2NH})$ (III). In 30 mL of CH_3CN was dissolved 0.40 g (1.1 mmol) of $Re(CO)_5Cl$. To this solution were added 0.20 g (1.0 mmol) of $[BrCH_2CH_2NH_3]Br$ and 0.07 mL (1.3 mmol) of aziridine consecutively, and the mixture was stirred for 10 min. At the end of this time, an IR spectrum of the solution did not reveal any bands due to $Re(CO)_5Cl$. The solvent was removed under vacuum. The white residue was dissolved in CH_2Cl_2, and the solution was evaporated to dryness to ensure complete removal of unreacted aziridine. The residue was extracted with CH_2Cl_2, the extract was filtered through anhydrous $MgSO_4$, and the volume of the filtrate was reduced under vacuum. Adding pentane and allowing the mixture to stand at −20 °C overnight produced snow white long needles. These were collected, washed with pentane, and vacuum dried: yield 0.38 g (85%); mp 135 °C. Anal. Calcd for $C_7H_5ClNO_5Re$: C, 20.77; H, 1.24; N, 3.46. Found: C, 21.41; H, 1.34; N, 3.57.

$Re(CO)_4Br(\overline{COCH_2CH_2NH})$ (IV). A mixture of 0.2 g (0.5 mmol) of $Re(CO)_5Br$, 0.03 mL (0.6 mmol) of aziridine, and 0.1 g (0.5 mmol) of $[BrCH_2CH_2NH_3]Br$ in 10 mL of CH_3CN was stirred for 10–15 min. After vacuum removal of the volatiles, the residue was extracted with CH_2Cl_2, the extract was filtered through $MgSO_4$, the filtrate was concentrated under vacuum, and the compound was precipitated from CH_2Cl_2–pentane at −20 °C as colorless long needles: yield 0.20 g (89%); mp 140 °C. Anal. Calcd for $C_7H_5BrNO_5Re$: C, 18.72; H, 1.12; N, 3.12. Found: C, 18.80; H, 1.09; N, 2.98.

The same compound was also prepared from the reaction of $Re(CO)_5Br$ (0.2 g, 0.5 mmol) with excess aziridine (0.075 mL, 1.50 mmol) in CH_3CN solvent without using the bromide salt $[BrCH_2CH_2NH_3]Br$. After 6 h of reaction, the product was crystallized as above to give 0.16 g (71%) of colorless crystals.

In another variation of this method using CH_2Cl_2 as the solvent in place of CH_3CN and $[BrCH_2CH_2CH_2NH_3]Br$ instead of $[BrCH_2CH_2NH_3]Br$, 0.23 g (83%) of snow white crystals of IV were obtained from 0.25 g (0.62 mmol) of $Re(CO)_5Br$ and 0.032 g (0.62 mmol) of aziridine. In all cases, the compounds were characterized as IV by IR and ^1H and ^{13}C NMR spectra.

$Re(CO)_4I(\overline{COCH_2CH_2NH})$ (V). This compound was prepared by the analogous method used for the preparation of IV. Starting with 0.22 g (0.49 mmol) of $Re(CO)_5I$ in 10 mL of CH_3CN, 0.10 g (0.49 mmol) of $[BrCH_2CH_2NH_3]Br$, and 0.026 mL (0.50 mmol) of aziridine, 0.17 g (71%) of colorless crystals of V were obtained from a CH_2Cl_2–hexane mixture at −20 °C; mp 80 °C. Anal. Calcd for $C_7H_5INO_5Re$: C, 16.94; H, 1.02; N, 2.82. Found: C, 16.74; H, 1.04; N, 2.84.

$Mn(CO)_4Cl(\overline{COCH_2CH_2O})$ (VI). A mixture of 0.27 g (1.2 mmol) of $Mn(CO)_5Cl$, 2 mL of $BrCH_2CH_2OH$, 0.11 g (1.1 mmol) of NaBr, and 20 mL of oxirane was stirred at 0 °C for 4 h. The stirring was then continued while the temperature of the bath was allowed to rise slowly to room temperature. After 16 h of reaction time, the volatiles were removed under vacuum to yield a pasty yellow mass. This was extracted with CH_2Cl_2 and filtered. An IR spectrum of this filtrate showed that almost all the starting complex had reacted. This solution was chromatographed on silica gel and eluted with CH_2Cl_2. The first yellow band contained a trace of unreacted $Mn(CO)_5Cl$. The second large orange-yellow band was collected and evaporated under a water aspirator vacuum to dryness. The residue was dissolved in CH_2Cl_2 and filtered, and the filtrate was concentrated. Long yellow needles of VI were obtained by adding 10 mL of hexane and allowing the mixture to stand at −20 °C overnight. The product crystals were collected, washed with hexane, and vacuum dried; yield 0.22 g (69%). The compound was characterized by its IR and ^1H[19] and ^{13}C NMR spectra.

$Mn(CO)_4Br(\overline{COCH_2CH_2O})$ (VII). A solution of 0.32 g (1.2 mmol) of $Mn(CO)_5Br$ in 8 mL of oxirane containing 1 mL of $BrCH_2CH_2OH$ and 0.1 g (1 mmol) of NaBr was stirred at 0 °C for 18 h. At the end of this period, no carbonyl bands of the parent compound were seen in the IR spectrum of the reaction mixture. Evaporation of the solution, extraction of the yellow residue with CH_2Cl_2, and filtration of the extract through anhydrous $MgSO_4$ followed by solvent removal under vacuum produced a yellow oil from which yellow crystals were obtained by adding pentane at −20 °C: yield 2.4 g (65%); mp 105 °C. Anal. Calcd for $C_7H_4BrO_6Mn$: C, 26.35; H, 1.24. Found: C, 26.44; H, 1.27. This compound was identical with that prepared by Stone et al.[19] by a different route.

$Mn(CO)_4I(\overline{COCH_2CH_2O})$ (VIII). To a solution of 0.1 g (0.3 mmol) of $Mn(CO)_5I$ in 5 mL of CH_3CN containing 1 mL of $BrCH_2CH_2OH$ held in an ice bath (0 °C) was added 5 mL of oxirane followed by 0.05 g (0.3 mmol) of NaI. The mixture was stirred for 2 h. All the volatiles were removed under vacuum. The residue was extracted with CH_2Cl_2, the extract was filtered through $MgSO_4$, and the solution was concentrated under vacuum. After pentane was added to this solution, it was allowed to stand at −20 °C. After 2 h long yellow needles were formed. These were collected, washed with pentane, and vacuum dried; yield 0.089 g (79%). The compund was characterized by IR and ^1H[19] and ^{13}C NMR spectra.

$Re(CO)_4Cl(\overline{COCH_2CH_2O})$ (IX). To a mixture of 0.10 g (1.0 mmol) of NaBr in 2 mL of $BrCH_2CH_2OH$ and 20 mL of oxirane at 0 °C was added 0.44 g (1.2 mmol) of $Re(CO)_5Cl$. The mixture was stirred at first at 0 °C for 3 h, and then the temperature of the bath was allowed to increase to room temperature. After the mixture

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(19) Bowen, D. H.; Green, M.; Grove, D. M.; Moss, J. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1189.

was stirred 16 h, its IR spectrum did not reveal any bands due to unreacted $\mathrm{Re(CO)_5Cl}$. The solvents were removed under vacuum, and the residue was taken almost to dryness. This was extracted with a large excess (70–100 mL) of $\mathrm{CH_2Cl_2}$, and the extract was filtered through $\mathrm{MgSO_4}$. The filtrate was taken to dryness by vacuum evaporation. The crude compound (yield 0.46 g (82%)) was extracted with $\mathrm{CH_2Cl_2}$, and the $\mathrm{CH_2Cl_2}$ solution was chromatographed on a silica gel column by using $\mathrm{CH_2Cl_2}$ as the eluent. The elution process was monitored by running IR spectra of the solutions. When all the compound had been eluted, the solvent was removed under a water aspirator vacuum. The residue was dissolved in $\mathrm{CH_2Cl_2}$, the solution was filtered, and white needles of the product were obtained from $\mathrm{CH_2Cl_2}$–pentane at −20 °C. These were collected, washed with pentane, and vacuum dried; yield 0.32 g (65%). Anal. Calcd for $\mathrm{C_7H_4ClO_6Re}$: C, 20.72; H, 0.99. Found: C, 20.97; H, 1.01.

$\mathrm{Re(OC)_4Br(\overline{COCH_2CH_2O})}$ (X). A mixture of 0.40 g (0.99 mmol) of $\mathrm{Re(CO)_5Br}$, 2 mL of $\mathrm{BrCH_2CH_2OH}$, 10 mL of oxirane, and 0.10 g (0.10 mmol) of NaBr was stirred at 0 °C for 6 h. When the reaction was complete (IR evidence), the solution was taken to dryness under vacuum. The residue was extracted with $\mathrm{CH_2Cl_2}$, the extract was filtered through anhydrous $\mathrm{MgSO_4}$, and the filtrate volume was reduced under vacuum until crystallization began. Addition of 10–15 mL of hexane and allowing the mixture to stand at −20 °C overnight produced colorless crystals that were collected, washed with hexane, and vacuum dried: yield 0.41 g (93%); mp 150 °C. Anal. Calcd for $\mathrm{C_7H_4BrO_6Re}$: C, 18.68; H, 0.89. Found: C, 18.99; H, 0.94.

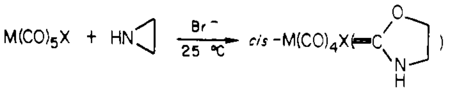
$\mathrm{Re(CO)_4I(\overline{COCH_2CH_2O})}$ (XI). Employing the same method of preparation as for X, we obtained 0.10 g (92%) of XI from 0.12 g (0.26 mmol) of $\mathrm{Re(CO)_5I}$, 0.02 g (0.2 mmol) of NaBr, 10 mL of oxirane, and 1 mL of $\mathrm{BrCH_2CH_2OH}$; mp 138 °C. Anal. Calcd for $\mathrm{C_7H_4IO_6Re}$: C, 16.91; H, 0.81. Found: C, 17.19; H, 0.83.

$\mathrm{Re(CO)_3Cl(\overline{COCH_2CH_2O})_2}$ (XII). This compound was obtained as a byproduct during the preparation of IX. Initial steps in this synthesis were the same as those described for IX. The residue left after the first $\mathrm{CH_2Cl_2}$ extraction was shaken with $\mathrm{CH_3CN}$ at 30–40 °C. This $\mathrm{CH_3CN}$ extract was then added to the silica gel column from which compound IX had been obtained earlier with $\mathrm{CH_2Cl_2}$. Compound XII was then eluted with $\mathrm{CH_3CN}$; the $\mathrm{CH_3CN}$ was evaporated under water aspirator vacuum to yield the microcrystalline compound. It was redissolved in a 1:1 $\mathrm{CH_3CN{:}CH_2Cl_2}$ mixture; the solution was filtered and concentrated by evaporation. When pentane was added and the mixture allowed to stand at −20 °C overnight, colorless crystals of XII formed. Starting from 0.36 g (0.98 mmol) of $\mathrm{Re(CO)_5Cl}$, 0.08 g (18%) of XII was obtained; mp 185 °C. Anal. Calcd for $\mathrm{C_9H_8ClO_7Re}$: C, 24.03; H, 1.79. Found: C, 24.78; H, 2.09.

$\mathrm{Mn(CO)_3Cl(H\overline{NCH_2}CH_2)_2}$ (XIII). To 20 mL of $\mathrm{CH_3CN}$ was added 0.06 g (1 mmol) of NaCl followed by 0.06 mL (1 mmol) of aziridine. The mixture was stirred for 20 min, and 0.26 g (1.1 mmol) of $\mathrm{Mn(CO)_5Cl}$ was added. After the mixture was stirred for about 2 h, the $\mathrm{CH_3CN}$ solvent became opaque and another portion of 0.06 mL (1 mmol) of aziridine was added to the mixture. After it was stirred for 10–15 min, the IR spectrum showed no bands due to the starting complex, indicating that all of the $\mathrm{Mn(CO)_5Cl}$ had reacted. The solvent was removed under vacuum, the residue was extracted with $\mathrm{CH_2Cl_2}$, and the extract was filtered through anhydrous $\mathrm{MgSO_4}$. The filtrate volume was reduced to one-third its original volume when fine yellow crystals precipitated out. The solution was slightly warmed to redissolve the crystals, hexane was added, and the mixture was allowed to stand at −20 °C overnight. The crystals thus formed were collected, washed with hexane, and finally dried under vacuum; yield 0.21 g (71%). Anal. Calcd for $\mathrm{C_7H_{10}ClO_3Mn}$: C, 32.27; H, 3.87; N, 10.75. Found: C, 32.06; H, 3.86; N, 10.92.

Results and Discussion

Reactions of Aziridine with $\mathrm{M(CO)_5X}$ (M = Mn, Re). 5-Membered Cyclic Aminooxycarbene Complexes, *cis*-$\mathrm{M(CO)_4X(\overline{COCH_2CH_2NH})}$. In the presence of a halide salt, aziridine is observed to react with one CO group in the neutral carbonyl complexes $\mathrm{M(CO)_5X}$ in $\mathrm{CH_3CN}$ solvent at room temperature, yielding air-stable 5-membered cyclic aminooxycarbene compounds according to eq 3. While the manganese compounds, I and II, are obtained as yellow and orange-yellow crystals in yields of 39% and 66%, respectively, the rhenium complexes are isolated as colorless needles in yields greater than 70%. All the compounds are soluble in $\mathrm{CH_2Cl_2}$ and $\mathrm{CH_3CN}$ and slightly soluble in $\mathrm{Et_2O}$. The reactions of $\mathrm{Mn(CO)_5Br}$ and $\mathrm{Re(CO)_5Br}$ with $\mathrm{H\overline{NCH_2}CH_2}$ proceed equally well in the presence of either of the bromide salts $\mathrm{[Br(CH_2)_{\mathit{n}}NH_3]Br}$ where $n = 2$ or 3.



(3)

I: M = Mn, X = Br
II: M = Mn, X = I
III: M = Re, X = Cl
IV: M = Re, X = Br
V: M = Re, X = I

It is also observed that the reaction of aziridine with $\mathrm{M(CO)_5Br}$ depends upon the nature of the solvents and on the halide ion used as the catalyst. For example, in the noncoordinating solvent $\mathrm{CH_2Cl_2}$ and in the absence of added $\mathrm{Br^-}$ ion, aziridine fails to react with $\mathrm{Re(CO)_5Br}$; neither $\mathrm{Re(CO)_4Br(\overline{COCH_2CH_2NH})}$ (IV) nor any aziridine-substituted compound analogous to XIII (vide infra) is generated even after 6 h of reaction time at room temperature. However, as soon as a bromide salt, $\mathrm{[BrCH_2CH_2CH_2NH_3]Br}$, is added to the above reaction mixture, IV is formed in 83% yield.

When the reaction of aziridine with $\mathrm{M(CO)_5Br}$ is carried out in $\mathrm{CH_3CN}$ solvent without any added $\mathrm{Br^-}$ salt, compounds I and IV are formed in 80 and 71% yields, respectively. However, this reaction takes a longer time to complete and consumes aziridine, which is partly lost due to polymerization.[11,20] Presumably in this reaction, $\mathrm{Br^-}$ dissociates from $\mathrm{M(CO)_5Br}$ in the polar and coordinating $\mathrm{CH_3CN}$ solvent according to the equilibrium

$$\mathrm{M(CO)_5Br + CH_3CN \rightleftarrows [M(CO)_5(CH_3CN)]^+ + Br^-} \quad (4)$$

Though no studies of the equilibrium (4) have been reported, it is known[21-23] that under refluxing conditions $\mathrm{CH_3CN}$ displaces 2 CO groups and the bromide ion from $\mathrm{Mn(CO)_5Br}$, thus forming $\mathrm{[Mn(CO)_3(CH_3CN)_3]^+}$. The concentration of free $\mathrm{Br^-}$ generated in reaction 4 is apparently sufficient to catalyze the carbene-forming reactions. Thus, the overall mechanism of the reaction is that proposed earlier.[10,11] In the present system, the $\mathrm{Br^-}$ ion may either be added to the solution or arise from equilibrium 4. The likely occurrence of reaction 4 suggests that $\mathrm{[Mn(CO)_5(CH_3CN)]PF_6}$[15] may also react with $\mathrm{H\overline{NCH_2}CH_2}$ in the presence of a bromide salt, $\mathrm{[BrCH_2CH_2NH_3]Br}$, to generate I. Indeed, this reaction in $\mathrm{CH_3CN}$ solvent does produce $\mathrm{Mn(CO)_4Br(\overline{COCH_2CH_2NH})}$ and $\mathrm{Mn(CO)_5Br}$, which are characterized by their IR and NMR spectra. In this reaction, it is not clear whether $\mathrm{Mn(CO)_5(CH_3CN)^+}$ or $\mathrm{Mn(CO)_5Br}$ is involved in the carbene-forming step.

Reactions of some cationic manganese complexes with aziridine and $\mathrm{[BrCH_2CH_2NH_3]Br}$ in $\mathrm{CH_3CN}$ at 25 °C were tried. There was no reaction with *trans*-$\mathrm{[Mn(CO)_4(PPh_3)_2]^+}$. $\mathrm{[Mn(CO)_5(PPh_3)]^+}$ forms very light yellow crystals suspended in an oil. Although we were unable to isolate a pure compound, the IR spectrum of the crystals [IR ($\mathrm{CH_2Cl_2}$): ν(CO), 2098 m, 2020 sh, 2000 vs $\mathrm{cm^{-1}}$; δ(NH), 1587 w $\mathrm{cm^{-1}}$; ν(CN),

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[20] Dermer, O. C.; Ham, G. E. "Ethylenimine and Other Aziridines"; Academic Press: New York, 1969.

[21] Reimann, R. H.; Singleton, E. *J. Organomet. Chem.* **1973**, *59*, C24.

[22] Reimann, R. H.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1974**, 808.

[23] Treichel, P. M. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 4, p 30.

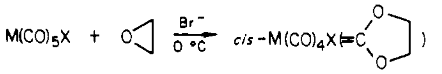
1530 m cm^{-1}] in the carbonyl stretching region compares well with those of $[\mathrm{Mn(CO)_4L(COCH_2CH_2CH_2)}]^+$ (L = a phosphine or arsine ligand)[24] complexes; this comparison suggests that the product might be the cationic species $[\mathrm{Mn(CO)_4(PPh_3)(COCH_2CH_2NH)}]^+$.

The reactions of aziridine with $\mathrm{Mn(CO)_5X}$ (X = Br, I) in the presence of bromide ($[\mathrm{BrCH_2CH_2NH_3}]\mathrm{Br}$) catalyst not only give aminooxycarbene products as the major component, but also forms another compound in trace amounts. This is demonstrated by the separation of the products of the reaction of $\mathrm{Mn(CO)_5I}$ with aziridine in the presence of $\mathrm{Br^-}$ on a silica gel column. The first eluted band contains traces of unreacted $\mathrm{Mn(CO)_5I}$, the second band affords the cyclic aminooxycarbene product II, and the last slow-moving yellow band yields a small amount of an oil whose IR spectrum in $\mathrm{CH_2Cl_2}$ exhibits three equally strong $\nu(\mathrm{CO})$ bands (2035 s, 1930 s, 1905 s, cm^{-1}) another band due to $\delta(\mathrm{NH})$ (1605 cm^{-1}), but not a medium–strong band at 1530 cm^{-1} for the $\nu(\mathrm{CN})$ of an aminooxycarbene ligand. The close similarity between this spectrum and that of *fac*-$\mathrm{Mn(CO)_3Cl(HNCH_2CH_2)_2}$ (vide infra) indicates that the compound is, most probably, *fac*-$\mathrm{Mn(CO)_3I(HNCH_2CH_2)_2}$, although it could not be isolated in pure form. Traces of a similar compound were also detected in the reaction of $\mathrm{Mn(CO)_5Br}$ with aziridine and $\mathrm{Br^-}$. However, in reactions of $\mathrm{Re(CO)_5X}$ with aziridine, no such product was observed. The much higher kinetic lability of the CO groups in $\mathrm{Mn(CO)_5X}$ as compared with $\mathrm{Re(CO)_5X}$ may be responsible for the difference in the Mn and Re systems.[25] Attempts to prepare $\mathrm{Mn(CO)_4Cl(COCH_2CH_2NH)}$ by the reaction of aziridine with $\mathrm{Mn(CO)_5Cl}$ in the presence of $\mathrm{Br^-}$ did not give a pure product. In the presence of either equimolar or a lesser amount of the bromide salt $[\mathrm{BrCH_2CH_2NH_3}]\mathrm{Br}$, this reaction always leads to a mixture of $\mathrm{Mn(CO)_4Cl(COCH_2CH_2NH)}$ and I. All efforts to separate this mixture were unsuccessful. IR and NMR spectra of the mixture also could not distinguish between the chloro and bromo analogues because of their very similar spectral features. However, elemental analyses of the sample and the detection of chloride as well as bromide ion by chemical methods demonstrate that it is a mixture of chloro and bromo derivatives. During the column chromatographic separation of the products of the reaction of $\mathrm{Mn(CO)_5Cl}$ with aziridine, a small amount of bright yellow crystals is obtained. They show IR bands in $\mathrm{CH_2Cl_2}$ at 2040 s, 1937 s, and 1905 s cm^{-1}. To establish the identity of this complex, $\mathrm{Mn(CO)_5Cl}$ was treated with aziridine in the absence (or the presence) of NaCl in $\mathrm{CH_3CN}$. This reaction affords the bis(aziridine)-substituted product *fac*-$\mathrm{Mn(CO)_3Cl(HNCH_2CH_2)_2}$ (XIII) instead of a cyclic carbene complex, (eq 5). This compound has been characterized by

$$\mathrm{Mn(CO)_5Cl + 2HNCH_2CH_2 \xrightarrow[25\ ^\circ C]{CH_3CN} \textit{fac}\text{-}Mn(CO)_3Cl(HNCH_2CH_2)_2} \quad (5)$$

IR, NMR, and elemental analyses. Its IR spectrum shows three almost equally strong $\nu(\mathrm{CO})$ bands in $\mathrm{CH_2Cl_2}$ solution at 2036 vs, 1936 vs, and 1904 vs cm^{-1} and another band at 1605 w cm^{-1} due to $\delta(\mathrm{NH})$; there is no $\nu(\mathrm{CN})$ band at 1530 cm$^-$ characteristic of the aminooxycarbene ligand.

Reactions of Oxirane with $\mathrm{M(CO)_5X}$ (M = Mn, Re). 5-Membered Dioxycarbene Complexes $\mathrm{M(CO)_4X(COCH_2CH_2O)}$ and $\mathrm{Re(CO)_3Cl(COCH_2CH_2O)_2}$. In the presence of $\mathrm{Br^-}$ ion and $\mathrm{BrCH_2CH_2OH}$ solvent at 0 °C, oxirane converts one CO group in $\mathrm{M(CO)_5X}$ to a cyclic dioxycarbene ligand according to eq 6. The air-stable products are obtained



(6)

VI: M = Mn, X = Cl
VII: M = Mn, X = Br
VIII: M = Mn, X = I
IX: M = Re, X = Cl
X: M = Re, X = Br
XI: M = Re, X = I

in high yields (65–79% manganese compounds; 65–93% rhenium compounds) as crystalline solids. The manganese compounds are yellow (Cl, Br) or orange-red (I) while the rhenium derivtives are all colorless. All are highly soluble in $\mathrm{CH_2Cl_2}$ andd $\mathrm{CH_3CN}$ but only slightly soluble in $\mathrm{Et_2O}$.

In the absence of NaBr, $\mathrm{M(CO)_5Br}$ (M = Mn, Re) did not react with oxirane in $\mathrm{BrCH_2CH_2OH}$ even after 18 h of reaction time. If the reaction of $\mathrm{Mn(CO)_5I}$ with oxirane is carried out in the presence of NaI, VIII is formed within 2 h; the use of $\mathrm{Br^-}$ requires a longer reaction time. The use of $\mathrm{BrCH_2CH_2CH_2OH}$ as the solvent instead of $\mathrm{BrCH_2CH_2OH}$ also affords $\mathrm{Re(CO)_4Br(COCH_2CH_2O)}$ in high yields. Stone and his co-workers[19] obtained the compounds $\mathrm{Mn(CO)_4X(COCH_2CH_2O)}$ (X = Cl, Br, I) in rather low yields (23–44%) as one of the products of the reaction of cationic carbene complexes $\mathrm{Mn(CO)_5(COCH_2CH_2O)^+}$ with LiX in $\mathrm{CH_3OH}$. The present procedure affords these carbene complexes in high yields in a single step.

The reaction of $\mathrm{Re(CO)_5Cl}$ with oxirane in the presence of $\mathrm{Br^-}$ results in the formation of $\mathrm{Re(CO)_4Cl(COCH_2CH_2O)}$ as the major product and a minor (18% yield) product $\mathrm{Re(CO)_3Cl(COCH_2CH_2O)_2}$, which are separated from each other by column chromatography or by repeated crystallization from $\mathrm{CH_2Cl_2}$ and washing with cold (0 °C) $\mathrm{CH_3CN}$. The bis(dioxycarbene) compound is difficultly soluble in $\mathrm{CH_2Cl_2}$ but is appreciably soluble in $\mathrm{CH_3CN}$. It may be noted that in contrast to the reaction of aziridine with $\mathrm{Mn(CO)_5Cl}$, which produces a mixture of both chloro and bromo derivatives, the oxirane reaction gives pure uncontaminated product, VI. The separation of products from the reaction of $\mathrm{Mn(CO)_5Cl}$, oxirane, and NaBr by chromatography yields, in addition to VI, a small amount of a greenish yellow oil, which shows three main IR bands in $\mathrm{CH_2Cl_2}$ (2038 s, 1965 s, 1930 s cm^{-1}) very similar to those of $\mathrm{Re(CO)_3Cl(COCH_2CH_2O)_2}$; however, the compound, presumably $\mathrm{Mn(CO)_3Cl(COCH_2CH_2O)_2}$, could not be obtained in a pure crystalline form because it undergoes decomposition.

In view of the formation of the bis(dioxycarbene) compound XII, the reactions of III with oxirane in $\mathrm{BrCH_2CH_2OH}$ containing NaBr at 0 °C and of X with aziridine in $\mathrm{CH_3CN}$ in the presence of $[\mathrm{BrCH_2CH_2NH_3}]\mathrm{Br}$ were performed with the hope of preparing mixed amino–oxy–dioxycarbene compounds. These reactions, however, did not produce the desired compounds.

General Trends in Reactivity. The present results along with those reported earlier[10,11] suggest that reactions 3 and 6 proceed by mechanisms (Schemes I and II in ref 11) that involve nucleophilic attack of aziridine (for reaction 3) and of $\mathrm{BrCH_2CH_2O^-}$ (or oxirane)(for reaction 6) on the carbon atom of a CO ligand; thus, the reactions depend on the electrophilicity of the CO group, which is indicated by the $\nu(\mathrm{CO})$ stretching force constant (calculated by the approximate method of

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[24] Game, C. H.; Green, M.; Moss, J. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 351.

[25] Zingales, F.; Graziani, M.; Faraone, F.; Belluco, U. *Inorg. Chim. Acta* **1967**, *1*, 172.

Table I. Important Infrared Bands (cm^{-1}) of Carbene and Other Pertinent Complexes in CH_2Cl_2 Solvent

compd	ν(CO)	δ(NH)	ν(CN)	compd	ν(CO)
$Mn(CO)_4Br(\overline{COCH_2CH_2N}H)$ (I)	2098 m, 2016 s, 1963 s	1607 w	1530 m	$Mn(CO)_4I(\overline{COCH_2CH_2O})$ (VIII)	2098 m, 2018 vs, 1976 s
$Mn(CO)_4I(\overline{COCH_2CH_2N}H)$ (II)	2091 m, 2009 vs, 1963 s	1605 w	1528 m	$Re(CO)_4Cl(\overline{COCH_2CH_2O})$ (IX)	2120 m, 2019 vs, 1948 s
$Re(CO)_4Cl(\overline{COCH_2CH_2N}H)$ (III)	2114 m, 2008 vs, 1941 s	1606 w	1530 m	$Re(CO)_4Br(\overline{COCH_2CH_2O})$ (X)	2116 m, 2016 vs, 1950 s
$Re(CO)_4Br(\overline{COCH_2CH_2N}H)$ (IV)	2110 m, 2004 vs, 1945 s	1600 w	1535 m	$Re(CO)_4I(\overline{COCH_2CH_2O})$ (XI)	2113 m, 2014 vs, 1954 s
$Re(CO)_4I(\overline{COCH_2CH_2N}H)$ (V)	2108 m, 2004 vs, 1946 s	1600 w, br	1530 m	$Re(CO)_3Cl(\overline{COCH_2CH_2O})_2$ (XII)	2044 vs, 1963 vs, 1908 vs
$Mn(CO)_4Cl(\overline{COCH_2CH_2O})$ (VI)	2106 m, 2027 vs, 1966 s			$Mn(CO)_3Cl(H\overline{NCH_2C}H_2)_2$ (XIII)	2036 vs, 1936 vs, 1904 vs
$Mn(CO)_4Br(\overline{COCH_2CH_2O})$ (VII)	2104 m, 2024 vs, 1972 s				

Cotton and Kraihanzel or given in the literature[26,27]).[28,29] Complexes in which a CO ligand is known to react with aziridine or oxirane in the presence of a halide catalyst are as follows (k(CO) (mdyn/Å) given in parentheses): $CpFe(CO)_3^+$ (17.60), $CpRu(CO)_3^+$ (17.60), $CpMn(NO)(CO)_2^+$ (17.80), $CpMn(NO)(CO)(\overline{COCH_2CH_2O})^+$ (17.14), $CpFe(CO)_2(\overline{COCH_2CH_2O})^+$ (17.16), $Mn(CO)_5Cl$ (16.27, 17.63), $Mn(CO)_5Br$ (16.31, 17.53), $Mn(CO)_5I$ (16.33, 17.41), $Re(CO)_5Cl$ (15.98, 17.47), $Re(CO)_5Br$ (16.10, 17.45), $Re(CO)_5I$ (16.11, 17.39). $Cr(CO)_6$ and $W(CO)_6$ (16.49, 16.41, respectively) do not react with $\overline{YCH_2CH_2}$ (Y = NH, O) under the same reaction conditions. It appears that the reactivity pattern of carbonyl complexes with $\overline{YCH_2CH_2}$ follows closely that of amines and alkoxide ions with these complexes, yielding carbamoyl and alkoxycarbonyl derivatives, respectively.[28] Those complexes that have k(CO) values ≥ 17.0 mdyn/Å are observed to react with $\overline{YCH_2CH_2}$, forming cyclic carbenes, and those having k(CO) < 17.0 mdyn/Å do not seem to react with the heterocycles, at least not at room temperature or below. Thus, another CO group in mono(aminooxycarbenes)[11] $CpFe(CO)_2(\overline{COCH_2CH_2N}H)^+$ (16.82) or $CpMn(CO)(NO)(\overline{COCH_2CH_2N}H)^+$ (16.89) having ν(CO) stretching force constants less than 17.0 mdyn/Å does not react with another mole of $H\overline{NCH_2C}H_2$ to form bis(aminooxycarbene) derivatives, whereas the corresponding dioxycarbene compounds,[11] namely $CpFe(CO)_2(\overline{COCH_2CH_2O})^+$ (17.16) and $CpMn(CO)(NO)(\overline{COCH_2CH_2O})^+$ (17.17), having k(CO) values greater than 17.0 mdyn/Å do react with oxirane to form bis(dioxycarbene) products. Similarly, $M(CO)_4X(\overline{COCH_2CH_2N}H)$ did not react further with $H\overline{NCH_2C}H_2$, whereas $Re(CO)_4Cl(\overline{COCH_2CH_2O})$, and probably also $Mn(CO)_4Cl(\overline{COCH_2CH_2O})$, are converted to the bis(dioxycarbene) derivatives in excess oxirane. While the k(CO) values may serve as a useful guideline in determining the trend in reactivity, other factors such as reaction conditions (high pressure and temperature), choice of catalysts, and kinetics certainly play a role in these conversions.

Table II. ^1H NMR Data (δ) of Carbene Complexes in CD_3CN

compd	$-OCH_2-$	$-NHCH_2-$	NH
I	4.72 (t)	3.71 (t)	9.15
II	4.67 (t)	3.69 (t)	8.97
III	4.68 (t)	3.69 (t)	9.10
IV	4.66 (t)	3.69 (t)	9.01
V	4.60 (t)	3.69 (t)	8.89
VI	4.76		
VII	4.76		
VIII	4.73		
IX	4.76		
X	4.76		
XI	4.74		
XII	4.68		
XIII		2.27, 1.96[a]	[b]

[a] Ring $-CH_2-$ of the two coordinated aziridines. [b] Not observed.

Table III. ^{13}C NMR Data (δ) of Carbenes in CD_3CN

compd	carbene C	CO	$-OCH_2-$	$-HNCH_2-$
I	231.68[a]	219.46, 212.00[a]	73.84	45.33
II	[b]	[b]	73.50	46.02
III	210.27	189.81, 186.87, 185.65	73.33	45.24
IV	208.19	188.60, 186.09, 185.13	73.24	45.59
V	205.07	186.52, 184.87, 184.27	73.06	45.94
VI	[b]	[b]	73.24	
VII	[b]	[b]	73.24	
VIII	[b]	[b]	73.24	
IX	225.87	188.60, 186.35, 184.61	73.32	
X	224.31	187.21, 185.39, 184.01	73.33	
XI	222.40	185.31, 183.92, 183.14	73.32	
XII	231.24	195.19, 190.42	72.20	
XIII		[b]		24.27, 23.40[c]

[a] Uncertain assignment due to low signal to noise ratio. [b] Not observed. [c] Ring $-CH_2-$.

Spectroscopic Characterizations. All the compounds are characterized by their IR and ^1H and ^{13}C NMR spectral data, which are given in Tables I–III, respectively. The IR spectral features of the $M(CO)_4X(\overline{COCH_2CH_2Y})$ compounds are very similar. They exhibit three ν(CO) absorptions in the region 2100–1940 cm^{-1}; the highest energy band at 2100 cm^{-1} is the

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(26) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.
(27) Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 702.
(28) Angelici, R. J.; Blacik, L. J. *Inorg. Chem.* **1972**, *11*, 1754.
(29) Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1691.

weakest while the band around 2025–2005 cm^{-1} is the strongest in intensity. The complexes $M(CO)_4X(\overline{COCH_2CH_2Y})$ have been assigned cis structures, which should give rise to four IR-active carbonyl bands.[30] But, as is frequently observed, solution IR spectra of the $M(CO)_4XL$ complexes[31,32] often show only three carbonyl bands as noted for carbene compounds I–XI. The tricarbonyl compounds XII and XIII also exhibit three ν(CO) bands, which closely resemble the pattern observed for other known *fac*-$M(CO)_3XI_2$ complexes, suggesting that XII and XIII have facial configurations.[33]

As observed earlier for cationic aminooxycarbene complexes,[11] the aminooxycarbene ligand in compounds I–V gives rise to two bands in the region 1600–1530 cm^{-1}: one that appears as a weak sometimes broad absorption has been assigned to the NH deformation mode, δ(NH); the other low-energy band of medium intensity is assigned to ν(CN) of the carbene ligand. Like $[CpFe(CO)_2(H\overline{NCH_2CH_2})]PF_6$[11] the IR spectrum of the bis(aziridine) compound XIII has a δ(NH) band at ~1600 cm^{-1}; it does not exhibit a band near ~1530 cm^{-1}.

The carbonyl stretching frequencies of the series of complexes $M(CO)_4X(\overline{COCH_2CH_2Y})$ containing the same metal ion decrease as Y changes from O to NH, implying that the π-acceptor/σ-donor ratio of the aminooxycarbene ligand is less than that of the dioxycarbene ligand. A similar trend has been observed in other cyclic carbene compounds such as $CpM(CO)_2(\overline{COCH_2CH_2Y})^+$ (M = Fe, Ru),[11] $CpMn(CO)(NO)(\overline{COCH_2CH_2Y})^+$,[11] and $CpFe(CO)(PPh_3)(\overline{COCH_2CH_2Y})^+$ [11] as well as in the acyclic carbene derivatives $CpFe(CO)_2[C(OMe)_2]^+$ [34,35] and $CpFe(CO)_2[C(OMe)NH_2]^+$.[36] In the compounds $M(CO)_4XL$ (L = a cyclic ligand) containing different halides but the same metal ion and the same L, the ν(CO) values are very similar in magnitude and are affected only modestly as X varies from Cl$^-$ to I$^-$.

^1H NMR spectra of the *cis*-$M(CO)_4X(\overline{COCH_2CH_2NH})$ complexes give rise to two triplets (AA′BB′ type) due to the $-OCH_2-$ (4.72–4.60 ppm) and $-NCH_2-$ (3.71–3.69 ppm) protons. The latter triplet has additional fine structure due to coupling with the NH proton. This has been proven by a decoupling experiment performed with *cis*-$Re(CO)_4Br(\overline{COCH_2CH_2NH})$. A similar coupling was observed earlier for the $CpM(CO)_2(\overline{COCH_2CH_2NH})^+$ (M = Fe, Ru)[11] complexes. The dioxycarbene compounds $M(CO)_4X(\overline{COCH_2CH_2O})$ show only a singlet at 4.76–4.73 ppm due to the $-OCH_2-$ protons of the carbene ligand. The chemical shifts of the methylene protons in both series of complexes *cis*-$M(CO)_4X(\overline{COCH_2CH_2Y})$ (Y = NH, O) show no appreciable changes in their values on replacing Mn with Re. The NH proton resonances of the aminooxycarbene ligands appear as broad signals in the low-field region (ca. 9.0 ppm).

Compound XIII exhibits two unequal, broad $-CH_2-$ signals at 2.27 and 1.96 ppm due to the two aziridine ligands coordinated to the metal. Since only one CH_2 resonance was expected for XIII, it seemed possible that aziridine had converted to another form. However, when excess PPh_3 is added to a CD_2Cl_2 solution of XIII, the two CH_2 signals disappear and a new broad weak ^1H signal appears at 1.8 ppm, which may be assigned to the $-CH_2-$ protons of free aziridine.[20] This experiment, which probably results in the formation of $Mn(CO)_3(PPh_3)_2Cl$ and the liberation of free aziridine, suggests that the aziridine ligands in XIII have not been converted into another ligand, which gives rise to the two ^1H signals. The ^{13}C NMR spectrum (Table III) of this compound also shows two ^{13}C signals for the $-CH_2-$ groups, the lower field signal being of greater intensity. These two signals might be due to the presence of two isomers. On the basis of the IR spectrum of XIII, one cannot exclude the possibility that a small amount of a *mer* isomer (cis or trans), as well as the *fac*, is present. As seen from literature data for *fac*- and *mer*-$M(CO)_3L_2X$ (M = Mn, Re; L = a phosphine or phosphite ligand),[33] the two carbonyl absorptions in the *mer* isomer that occur below 2000 cm^{-1} appear at almost the same positions as the two lower ν(CO) bands in the *fac* isomer.

The proton NMR spectrum of XII, which has two cyclic dioxycarbene ligands, contains only one $-OCH_2-$ signal, which lies at slightly higher field in comparison to those observed for IX – XI. The observation of a singlet for the OCH_2 groups suggests that at room temperature on the NMR time scale the methylene protons of the dioxycarbene rings are equivalent due to rapid rotation around the Re=C bond. The low-temperature NMR spectrum of the compound could not be obtained because of its low solubility.

In ^{13}C NMR spectra of the *cis*-$Mn(CO)_4X(\overline{COCH_2CH_2Y})$ complexes, no carbene nor carbonyl resonances could be detected probably because of quadrupolar broadening by the ^{55}Mn nucleus.[37,38] Attempts to observe these resonances by accumulating data at lower temperatures were unsuccessful because of the insolubility of the compounds. Only in the case of *cis*-$Mn(CO)_4Br(\overline{COCH_2CH_2NH})$ in CD_2Cl_2 at −10 °C could we detect one carbene ^{13}C and two carbonyl ^{13}C signals (instead of the expected three CO resonances). For the rhenium carbene complexes, all four ^{13}C resonances for the carbene and carbonyl ligands are observed. The ^{13}C signals appearing at low field (greater than 200 ppm) demonstrate conclusively the presence of the carbene carbon in the rhenium compounds (III–V and IX–XI). The ^{13}C resonances of the carbene carbon in the cyclic aminooxy ligand occur at higher field than those in the cyclic dioxy group. One observes a similar trend in other carbonyl complexes containing cyclic and acyclic aminooxy- and dioxycarbene ligands.[11,33–35]

The ^{13}C resonances for the $-OCH_2-$ and $-NCH_2-$ carbons of the aminooxycarbene groups in the rhenium complexes occur at ca. 73 ppm and at ca. 45 ppm, respectively; in the dioxycarbene ligands, the $-OCH_2-$ ^{13}C signal appears at ~73 ppm. In the manganese compounds these ^{13}C signals, which have almost the same chemical shift as observed for the rhenium complexes, may be taken as evidence for the presence of aminooxy- and dioxycarbene ligands.

All the rhenium compounds *cis*-$Re(CO)_4X(\overline{COCH_2CH_2Y})$, where Y = NH or O, give rise to three ^{13}C peaks with relative intensities of 1:2:1, which are expected for the three kinds of CO groups in the cis geometry of this complex. In the aminooxycarbene as well as the dioxycarbene compounds, corresponding CO resonances move upfield (Table III), with a change of the halo ligand in the order Cl < Br < I. The carbene ^{13}C resonances in the same complexes also move upfield in the same order. However, the $-OCH_2-$ and $-NCH_2-$ carbon signals remain unchanged, indicating that the halo ligands have a significant influence only on those

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(30) Haines, L. M.; Stiddard, M. H. B. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 53.

(31) Angelici, R. J.; Basolo, F. *J. Am. Chem. Soc.* **1962**, *84*, 2495.

(32) Angelici, R. J.; Denton, D. L. *Inorg. Chim. Acta* **1968**, *2*, 3.

(33) Bond, A. M.; Colton, R.; McDonald, M. E. *Inorg. Chem.* **1978**, *17*, 2842.

(34) Quick, M. H.; Angelici, R. J. *J. Organomet. Chem.* **1978**, *160*, 231.

(35) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 1111.

(36) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 1118.

(37) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *80*, C31.

(38) Webb, M. J.; Graham, W. A. G. *J. Organomet. Chem.* **1975**, *93*, 119.

Inorg. Chem. **1984**, *23*, 2705–2708 **2705**

carbon atoms that are directly bonded to the metal.

Registry No. I, 90968-72-2; II, 90968-73-3; III, 90968-74-4; IV, 90968-75-5; V, 90968-76-6; VI, 40901-27-7; VII, 53821-91-3; VIII, 53821-89-9; IX, 41121-63-5; X, 90990-45-7; XI, 90990-46-8; XII, 90968-77-7; XIII, 90968-78-8; $[BrCH_2CH_2NH_3]Br$, 2576-47-8; $Mn(CO)_5Br$, 14516-54-2; $Mn(CO)_5I$, 14879-42-6; $Re(CO)_5Cl$, 14099-01-5; $Re(CO)_5Br$, 14220-21-4; $[BrCH_2CH_2CH_2NH_3]Br$, 5003-71-4; $Re(CO)_5I$, 13821-00-6; $Mn(CO)_5Cl$, 14100-30-2; $BrCH_2CH_2OH$, 540-51-2; NaBr, 7647-15-6; NaCl, 7647-14-5; $Re_2(CO)_{10}$, 14285-68-8; $[Re(CO)_5(CH_3CN)]PF_6$, 55057-83-5; NaI, 7681-82-5; aziridine, 151-56-4; oxirane, 75-21-8.

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Reactivity of *cis*-Diamminebis(dimethyl sulfide)platinum(II) Perchlorate

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The reaction between *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ and a range of anionic nucleophiles has been studied in aqueous solution at 25.0 °C by using a combination of absorption spectrophotometry and ^1H NMR measurements. In all cases, the first leaving group is ammonia and the relative second-order constants are Cl^- (1) < NO_2^- (2.4) < N_3^- (3.7) < Br^- (5.6) < SCN^- (260) < I^- (480). In all cases a second anion enters in a subsequent step, displacing ammonia in the case of Cl^-, Br^-, and I^- and dimethyl sulfide in the case of NO_2^-, N_3^-, and SCN^-. It is suggested that the relatively high trans effect of dimethyl sulfide is the main factor that determines the leaving group in the first stage of the reaction.

Introduction

In our studies of the factors that determine the reactivities of four-coordinate complexes of platinum(II), we have found that, contrary to the early suggestions of Basolo and Pearson,[3] the charge of the substrate plays an important part in determining the reactivity of the complexes and the relative nucleophilicity of the entering groups. For example, whereas the original $n_{Pt}°$ nucleophilicity scale[4] can be applied quite well to substrates of the same charge type as the standard *trans*-$[Pt(py)_2Cl_2]$ (py = pyridine), there are a number of nucleophiles whose reactivities are significantly greater or less than those predicted on the basis of their $n_{Pt}°$ values when they enter an ionic or cationic substrates, respectively. Such species were termed "biphilic"[5] in accordance with a hypothesis that they owed part of their reactivity to their ability to function additionally as π acids, and one might therefore expect that their reactivity relative to that of pure σ bases might change according to the π basicity of the reaction center. It has been shown that, by using a new standard substrate, $[Pt(en)(NH_3)Cl]^+$ (en = 1,2-diaminoethane), a nucleophilicity scale that applies very well to 1+ cationic substrates can be developed,[6] and more recently, Romeo[7] has extended this approach to assign a standard to 2+ cationic substrates. The number of dipositive Pt(II) substrates whose reactivity is sufficiently large to allow a detailed study of their reactions with a wide range of nucleophiles is quite restricted, and the first purpose of the work reported in this paper was to extend the number of dicationic species studied.

Apart from H_2O and alcohols, neutral ligands are generally poor nucleofuges in polar solvents. This situation does not apply in nonpolar solvents such as dimethoxyethane, where complexes such as *cis*-$[Pt(Me_2S)_2Cl_2]$ react with neutral nucleophiles such as amines and lose the neutral ligand Me_2S[8] in spite of the fact that chloride is normally a good leaving group, especially under the moderate trans effect of Me_2S.[9] This is a consequence of the inability of the nonpolar solvents to facilitate ionogenic reactions, but the relatively high reactivity of this system is worth noting. The substrate reverts to normal behavior, i.e. loss of chloride, in polar solvents.[10] The complex *cis*-$[Pt(Me_2SO)_2Cl_2]$ also undergoes displacement of the neutral sulfoxide in 1,2-dimethoxyethane,[11] but in this case, the neutral ligand is also often displaced in aqueous and methanolic solutions as well.[12] Considerable attention is now being paid to this mutual labilization of a pair of cis sulfoxides, and it is of considerable interest to compare the behavior of sulfoxides and thioethers in this context. The two threads of interest, namely the nucleophilicity scales appropiate to dicationic complexes and the mutual labilization of a pair of cis sulfur donor ligands, come together in this work. We have synthesized the species *cis*-$[Pt(Me_2SO)_2(NH_3)_2]^{2+}$ and *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ in order to make this comparison with anionic nucleophiles in aqueous solution. The first undergoes reaction with the loss of dimethyl sulfoxide at a rate that requires a stopped-flow technique to follow it. The much slower reactions of the latter complex can be followed by classical methods and are reported in this paper.

Experimental Section

Preparations. *cis*-$[Pt(Me_2S)_2(NH_3)_2](ClO_4)_2$. *cis*-$[Pt(NH_3)_2Cl_2]$ (256.5 mg, 0.855 mmol), prepared by the method of Kauffman,[13] was suspended in methanol (65 cm^3); silver perchlorate (354.5 mg, 1.71 mmol) was added and the mixture stirred at room temperature for 24 h. The precipitated AgCl was filtered off and the filtrate treated with excess dimethyl sulfide (0.25 cm^3). After 1 h the solution was concentrated in a rotatory evaporator, and the required product was precipitated by addition of diethyl ether and dried under vacuum; yield 375 mg (79%). Anal. Calcd for $C_4Cl_2H_{18}N_2O_8S_2Pt$: C, 8.70; H,

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[1] Università di Venezia.

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[3] Basolo, F.; Pearson, R. G. "Mechanism of Inorganic Reactions"; Wiley: New York, 1958.

[4] Belluco, U.; Cattalini, L.; Basolo, F.; Pearson, R. G.; Turco, A. *J. Am. Chem. Soc.* **1965**, *87*, 241.

[5] Gray, H. B. *J. Am. Chem. Soc.* **1962**, *84*, 1548.

[6] Bonivento, M.; Cattalini, L.; Marangoni, G.; Michelon, G.; Schwab, A. P.; Tobe, M. L. *Inorg. Chem.* **1980**, *19*, 1743. Bonivento, M.; Canovese, L.; Cattalini, L.; Marangoni, G.; Michelon, G.; Tobe, M. L. *Ibid.* **1981**, *20*, 3728.

[7] Romeo, R.; Cusumano, M. *Inorg. Chim. Acta* **1981**, *49*, 167.

[8] Canovese, L.; Cattalini, L.; Marangoni, G.; Michelon, G.; Tobe, M. L. *Inorg. Chem.* **1981**, *20*, 4166.

[9] Kennedy, B. P.; Gosling, R.; Tobe, M. L. *Inorg. Chem.* **1977**, *16*, 1744.

[10] Cattalini, L., unpublished results.

[11] Bonivento, M.; Canovese, L.; Cattalini, L.; Marangoni, G.; Michelon, G.; Tobe, M. L. *Inorg. Chem.* **1981**, *20*, 1493.

[12] Braddock, P. D.; Romeo, R.; Tobe, M. L. *Inorg. Chem.* **1974**, *13*, 1170.

[13] Kauffmann, G. B.; Cowan, D. O. *Inorg. Synth.* **1963**, *7*, 239.

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